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UNIT 2A

SYLLABUS

CHLOR-ALKALI INDUSTRIES: Manufacture of caustic soda by membrane cell method, diaphragm cell and by lime soda process. Soda ash, sodium hypochlorite and chlorine

ALKALI AND CHLORINE

2.0 INTRODUCTION

Caustic soda, soda ash and chlorine are most important heavy chemical. Because their extensive use in a large number of industries and hardly a consumer product is sold that is not dependent at some stage of its manufacture on chlorine and alkalies.

Caustic soda is an important heavy chemical and occupies among the basic chemicals position equal in importance to sulfuric acid and ammonia. It is used in soap, rayon, dyes, paper, drugs, foods, rubber, textiles, chemicals, bleaching, metallurgy and petroleum industries.

Chlorine, which is obtained as byproduct in the manufacture of caustic soda, finds applications in paper and pulp, solvents, explosives, plastics, pesticides, sanitation and various chemical industries.

Sodium carbonate or soda ash, another alkali, has widely been used in soap, sugar, glass, drugs, dyes, paper, ceramics, textiles, metallurgy, chemicals, petroleum, leather, water softening industries, etc.

It is evident, therefore, that a large number of industries are dependent upon alkalies like NaOH and Na₂CO₃ and chlorine obtained as a byproduct. These are, therefore, prepared on a large scale.

Salt is the basic raw material for the caustic soda and chlorine, soda ash (sodium carbonate), sodium sulfate, hydrochloric acid etc. Salt is also used in a large number of other industries, such as hydrogenation of oil, manufacture of soap, dyes, textile, food processing etc.

So before proceeding for the manufacture of alkalies, let us gain some idea about the common salt which is used as the basic raw material for their manufacture.

2.1 COMMON SALT

Salt is most widely distributed inorganic compound throughout the world. It is a part of human food and life without salt is probably impossible. Other living beings, such as animals, also require salt for their growth. In India, about 70% of the salt is consumed by human being and rest 30% is used in the manufacture of alkalies and other industrial products like soaps, textiles, dyes etc.

2.1.1 Sources of common salt in India

(1) Sea Water: The main salt manufacturing centers from sea brine in India is Maharashtra, Gujarat, Tamilnadu, Kerala, Andhra Pradesh, Karnataka, Orissa and West Bengal. About 70% of the total salt production comes from sea water.

(2) Salt Lakes: There are two important salt lakes in India. Sambhar lake Rajasthan and chilka lake (on east coast). More than 2.5 lakh tones of common salt is produced every year from Sambhar lake.
(3) **Sub Soil Water:** It "contains more salt than the sea water" that is why, is becoming an important source of salt in the country. Kharagoda, Didwana, Dharangadhra and Tucticorin are the important centers in India, Where salt is manufactured from sub-soil water.

(4) **Rock Salt:** In Mandi (Himachal Pradesh) salt has also been manufactured from rock salt which is also used during religious festivals. India exports salt to various countries such as Japan, Nepal, Formosa, Srilanka and East Africa.

### 2.1.2 Methods of manufacture

Salt obtained from above sources is in solution or liquid form. This form is called as **brine.** The various methods used for concentrating the brine solutions are:

2. Artificial Evaporation.
3. Freezing method.

#### (1) Solar Evaporation

It is the cheapest and best method of manufacturing salt from the brines. This method has widely been used in India. In this method, the sea brine (3-3.5° Be) is first conveyed to a reservoir through channels to store brine, remove suspended impurities and to concentrate the brine from original 3-3.5° Be to about 10°Be by solar energy. The reservoir is usually kept at a certain height, where brine flows under gravity. The 10° Be brine is again concentrated to 25° Be brine by **solar evaporation** by passing it to condensers through the channels. Due to evaporation of water from brine the solution gradually concentrates and different impurities separate out at different concentration. Thus about 7.5° Be ferrous iron present separates out as ferric oxide. At 10° Be, calcium carbonate precipitates out, while at 12° Be, calcium sulfate also start precipitating. At about 25° Be nearly whole of the calcium sulfate separates out. The 25°Be brine from the **condensers** is now passed on to the **crystallizes,** where salt crystallizes from 25.4° Be to 30° Be and other impurities also start separating. The salt is scraped out and the mother liquor (bittern) is separated for the recovery of other by products. The main constituents of bittern are NaCl, MgCl₂, MgSO₄, KCl and Br₂.

Brine obtained from other sources can be similarly evaporated in order to get the pure salt. For every ton of salt made, about one ton of mother liquor (bittern) is produced. The various byproducts obtained from bitterns are bromine, magnesium salts such as magnesium chloride, mixed salts etc. Other byproducts of salt industry are calcium carbonate, calcium sulfate, potassium chloride, sodium sulfate etc.

#### (2) Artificial Evaporation

In cold countries, where solar evaporation is not possible on a large scale, artificial evaporation method is used. Combination of solar evaporation as well as artificial evaporation methods is also used in France and Germany. The brine obtained in these countries has been found to be very dilute.

Artificial evaporation was carried out in open pans but it is now carried out in vacuum pans, known as vacuum evaporation methods. It this method, brine is boiled under reduced pressure in vacuum pan in order to get cubical grains of salt.

Purified brine is pumped to the vacuum pans, where calcium sulfate is removed as a result of counter current flow and hydraulic washing with brine. The **vacuum pan evaporators** are usually **triple effect evaporators** made of cast iron steel sheets and copper tubes. Salt slurry is continuously drawn from each evaporator through the salt leg at the bottom of which brine is feed so that the salt slurry is washed by incoming brine, thus washing back the impurities into the pans. The salt slurry is then conveyed to a **cone shaped tank** from where it passes to **feed tank** for dewatering and drying. The filtered and partially dried salt from the feed tank (fitted with feeding rotary vacuum pump) finally goes to a rotary drier for final drying. The lumps of the dried salt are removed from fine dry crystals by passing through a scalping screen. The salt is then conveyed to storage bins, where it is screened, sized and packed.

#### (3) Freezing Method

In some countries, salt is also manufactured by freezing the brine, but it is not a common method.
2.2 CAUSTIC SODA

Caustic soda and chlorine are produced almost entirely as coproducts by the electrolysis of brine. The process accounts for 80% caustic soda and more than 95% of chlorine production in India. In the electrolysis of brine, chlorine is liberated at the anode and caustic soda together with hydrogen is produced at the cathode. In order to keep the anode and cathode products separate from one another various commercial cells have been developed. So before proceeding to the actual procedure, let us gain some idea about the cells to be used in the manufacturing of caustic soda.

2.3 TYPE OF CELLS

Two types of cells were used, Diaphragm cells and mercury cathode cells. But recently membrane cell is widely used for production of caustic soda. All the three types of cells have been divided to keep the anode compartment separated from the cathode compartment in order to prevent the reaction between chlorine and caustic soda formed respectively in anode and cathode compartments. Diaphragm and Membrane cells use diaphragm and semi-permeable membrane respectively for separation of the anode and cathode compartments.

2.3.1 Diaphragm cells
Diaphragm cells are two types.

(1) Submerged Cells
In these cells cathodes remain submerged; graphite is universally used as anode. The liquid in the cathode compartment is at low-level in order to prevent the back flow of OH⁻ ions by diffusion. Hooker and Townsend cells are well known examples of submerged diaphragm cells.

(2) Dry Diaphragm Cells
In these cells electrolysis starts with dry cathode compartment or empty cathode compartment. Graphic is used as an anode. Vorce, Nelson, Gibbs cells are the well-known examples of dry diaphragm cells.

The diaphragm cells contain a porous asbestos diaphragm to separate anode compartment from cathode component. This allows ions to pass through by electrical migration, but reduces diffusion of products. It permits a flow of brine from the anode to cathode and prevents the mixing of anode product and cathode products. Some of the important diaphragm cells used in the past and present are given below.

2.3.1.1 Submerged cell: Hooker cells
Hooker cells are most popular and widely used cells and vary capacity from 10000 amp to 55000 amp. The cell is cubic in shape. The cell has concrete cover at the base from which flat blades of the graphite projects upward and act as anodes. These are supported vertically by a layer of lead cast concrete base. In these types of cell, there are 90 such anodes, each measuring of 46 X 16 X 3 cm. The cathode consisting of flat steel fingers are supported horizontally from the side steel frame extending inwards, from two sides so as to fit between the rows of anode blades. The cell has concrete cover, which has inlet for brine and exit pipe for chlorine gas. This concrete cover also projects the cast lead forming the condenser to the anodes from attack by cell liquor. The cathode assembly has hydrogen and caustic off takes and the cathode connection. The cathode is directly covered with asbestos and forms the diaphragm, which is completely submerged. Diaphragm is very easy to apply on the cathode. The cathode is dipped into a bath of asbestos slurry and the asbestos is drawn into the screen by applying a vacuum to the hydrogen outlet.
The brine passes into the anode compartment of the cell through the concrete cover and liberated chlorine at the anode escapes through the cell cover. Hydrogen liberates at the steel cathodes and the weak brine containing caustic soda is withdrawn through the hollow rectangular channel frames at the side. A feed of brine between anode and cathode compartment maintains the separation of anode products from cathode products.

2.3.1.2 Dry/Porous diaphragm cells: Nelson cell

It consists of a perforated steel tube having a thin lining of asbestos on the inside. This steel tube acts as the cathode and is suspended in an outer steel tank. Brine is placed inside the cathode tube and a graphite rod is immersed in it. The graphite rod acts as anode. When an electric current is passed, the salt solution undergoes electrolysis and its ions pass through the diaphragm as a result of electrical migration. Hydrogen and caustic soda are formed at the cathode and chlorine at the anode. Hydrogen gas is allowed to escape through an opening provided at the top of the cell, while caustic soda is collected at bottom from where it can be withdrawn from time to time. Chlorine liberated at the anode is led away through a pipe and compressed into steel cylinders.

The space between the cathode and outer tank is kept full of steam, which acts in two ways.

1. It heats the electrolyte and thus reduces its resistance
2. Keeps the pores of the asbestos diaphragm clear which make migration of ions easy.

Sodium ions pass through the asbestos and reach the cathode, where H\(^+\) ions and OH\(^-\) ions are formed as a result of reduction of water. Hydrogen escapes through an opening at the top and Na\(^+\) ions combine with OH\(^-\) ions to form caustic soda, which is collected at the bottom of the outer tank

\[
\text{NaCl} \xrightarrow{\text{Reaction}} \text{Na}^+ + \text{Cl}^- \\
\text{At cathode} \xrightarrow{\text{2H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{OH}^-} \\
\text{At Anode} \xrightarrow{\text{Cl}^- - \text{e}^- \rightarrow \text{Cl}} \\
\text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH} \\
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2
\]

**2.3.2 Mercury cathode cells**

The method of producing chlorine and caustic soda in an electrolytic cell with mercury cathode was first introduced by Castner and Kellner in 1892.

**2.3.2.1 The Castner Kellner cell**

The cell consists of large rectangular tank with a layer of the mercury at the bottom and into three compartments by the state partition not touching the bottom of the cell. The mercury is kept in circulation from one compartment to another by means of eccentric wheel H. Each of the side compartments called A, A is fitted with graphite anodes dipping in brine, whereas a series of iron roads suspended in the middle compartment act as cathodes. The compartment contains a dilute solution of soda.

When the electric current is passed, the electrolysis of brine takes in the outer compartment A, A. Chlorine is liberated at the anode and is led away through an exit provided at the top. Sodium ions are discharged at the mercury layer which acts as cathode by induction. It should be noted that H\(^+\) ion will not be discharged because of high over potential over the mercury.

\[
\text{Na}^+ + \text{e}^- \rightarrow \text{Na} \text{ (At cathode)}
\]

The liberated sodium atoms dissolved in the mercury to from a sodium amalgam which comes into the central compartment due to the rocking motion given to the cell by eccentric wheel H. In the compartment the Hg layer acts as an anode. As a result of electrolysis of NaOH solution present in central compartment, OH\(^-\) ions and Na\(^+\) ions are formed. The OH\(^-\) ions move to the mercury anode and after getting discharged react with the sodium atom presents in the amalgam to form sodium hydroxide. At the same time, the H\(^+\) ions furnished by slight dissociation of water get discharged as hydrogen which escapes through exit above the middle compartment, the caustic soda solution is sufficiently concentrated (above 20%) it is removed periodically and concentrated to get fused caustic soda.

**2.3.3 Membrane cell**

Membrane cells use a semi-permeable membrane to separate the anode and cathode compartments. With diaphragm cells, back migration of ion is controlled by the rate of flow of fluids through the diaphragm and this is regulated by careful control of liquid level.
in the compartments. **Membrane cell** separates the compartments with porous chemically active plastic sheet that allow Na⁺ ion to pass but rejects the OH⁻ ions. **Several polymers** have been developed for these demanding services. **Du Pont** has developed persulfonic acid polymer (Nafion) while **Ashai** uses a multiple layer membrane of perfluorosulfonic acid polymer. The purpose of membrane is to exclude OH⁻ and Cl⁻ ions from the anode chamber, thus making the product far lower in salt than that from diaphragm cell.

Membrane cells operate using a more concentrated brine and produce a purer, more concentrated product (28% NaOH containing 50ppm of NaCl, 40% NaOH product has recently been claimed.) Such product requires only 715kg of water to be evaporated to produce a metric ton of 50% caustic, a considerable saving because of the difficulty and expenses of concentration and purification, only large diaphragm cells installation are feasible. Membrane cell producing relatively concentrated NaOH offer the possibility of operation at the point of caustic use, the saving freight. Small efficient units may cause a revolution in distribution of the chlor-alkali industries, particularly if efficiency remains high in small units.

Serious suggestion have been made that combination plant using the output of the membrane cells as fed to diaphragm cells might result in optimum application of both and make a considerable cost reduction overall. Such combinations have been used with mercury cell output feeding the diaphragm cells.

Membranes are more readily clogged than diaphragm, so some of the savings are lost because of necessity of pretreat the brine fed in order to remove calcium and magnesium before catalysis.

A membrane cell 20 times larger than diaphragm is being offered in 1981. Such a cell unit can produce 240 ton of chlorine per year and power consumption is satisfactory reduced below either mercury or diaphragm cells. A bipolar cell unit is capable of producing 20,000 ton per year with a current density of 4 KA/M².

### 2.4 MANUFACTURE OF CAUSTIC SODA AND CHLORINE USING DIAPHRAGM CELLS

#### 2.4.1 Raw material
The main raw material for the manufacture of caustic soda by electrolytic method is the common salt of required purity. In INDIA, this salt is found in various parts, such as Sambhar, Khragods, Saurashtra, Andhra, Tutecorin, Adhirampatanara etc.

#### 2.4.2 Brine purification
Commercial sodium chloride usually contains impurities such as calcium, magnesium and iron compounds. So, the brine purification is necessary for getting pure caustic soda and to decrease clogging of the cell diaphragm by insoluble hydroxides formed during electrolysis. These **impurities** are removed by adding lime and soda ash, when insoluble carbonates and hydroxides are precipitated. Sometimes sulfate are removed with BaCl₂ or the hot brine is treated with OH⁻ and CO₃²⁻ ions. The clear brine is neutralized with hydrochloric acid. After treatment for purification the brine is allowed to settle. The brine **saturated with NaCl** at 60°C is fed into the cell containing 324gms/liter of NaCl. The electrolysis is carried out in diaphragm cells; each cell usually required 3.0-4.5 volts. A number of them are put in series to increase the voltage of a given group.

#### 2.4.3 Brine Electrolysis
Brine electrolysis is carried out with an anode current density of 0.07amp/cm². As a result of electrolysis Na⁺ ions move to the cathode, where H⁺ ions and OH⁻ ions are also formed as a result of reduction of water. On the other hand Cl⁻ ions are directed towards the anode, where they lose one electron each and are thus liberated as chlorine atoms, which unite immediately to form chlorine molecules and hence chlorine gas at the anode. Since the discharge potential of chlorine ions is lower than that of OH⁻ ions, Cl⁻ ions are discharge at the anode and OH⁻ ions are remain in solutions. Similarly the discharge potential of Na⁺ is greater than H⁺ ions hence H⁺ ions are discharge at the cathode, while Na⁺ ions remain in the solutions.

\[
\text{NaCl} \xrightarrow{\text{ electrolysis}} \text{Na}^+ + \text{Cl}^- \\
2\text{H}_2\text{O} + 2\text{e}^- \xrightarrow{\text{ electrolysis}} \text{H}_2 + \text{OH}^- 
\]
At cathode

\[ \begin{align*}
2H_2O + 2e^- & \quad \leftrightarrow \quad H^+ + 2OH^- \\
Na^+ + OH^- & \quad \leftrightarrow \quad NaOH
\end{align*} \]

At Anode

\[ \begin{align*}
Cl^- - e^- & \quad \leftrightarrow \quad Cl \\
Cl^- + Cl^- & \quad \leftrightarrow \quad Cl_2
\end{align*} \]

Since chlorine attack caustic soda solution even in the cold, formed sodium chloride and hypochlorite, it is necessary that the construction of the cell should be such that NaOH and Cl\(^-\) once formed do not come in direct contact with one another.

\[ 2NaOH + Cl_2 \quad \rightarrow \quad NaCl + NaClO + H_2O \]

2.4.4 Evaporation and salt separation

The caustic soda solution obtained from the cell contains about 10 to 15% caustic soda and some unconverted NaCl. The decomposition efficiency of the cells being in the range of only 50%, about half of NaCl remains unconverted and is recovered by reason of its low solubility in caustic soda solutions after concentrations. Hence the weak caustic soda obtained from the electrolyte cell is first **concentrated to 50%** in a **double or triple effect evaporator** so that NaCl being less soluble and almost completely separated, particularly in the presence of caustic soda. The salt so recovered is used again. The liquid obtained from the salt separator is 50% caustic soda solution containing 2% NaCl and 0.1 to 0.5% NaCl on a dry basis.

2.4.5 Final Evaporation

The 50% NaOH solution is concentrated in huge cast iron pot on open fire. About 99% water is removed and molten caustic soda is formed. The final temperature is 500°C to 600°C. These pots have now been replaced by dowtherm heated **evaporators** for caustic evaporation about 50%. **Another method** of dehydrating 50% caustic soda is the **precipitation** of sodium hydroxide mono hydrate which contains much less water than the original solution. The precipitation may be carried out by adding ammonia to the 50% solution. These also purify the caustic soda. If 50% caustic soda is treated with **anhydrous ammonia** in pressure vessels in a counter current manner, free flowing anhydrous crystals of NaOH separate out from the resulting aqua ammonia.

The hot anhydrous caustic is treated with sulfur to precipitate iron and then allowed to settle. Then a centrifugal pump is lowered by crane in the molten NaOH and the liquid is pumped out in to thin steel drums.

2.4.6 Purification of caustic soda

50% caustic soda solution still contains impurities such as colloidal iron, NaCl and NaClO. Iron is removed by treating caustic with 1% by weight of 300mesh CaCO\(_3\) and filtering the resulting mixture through a filter on a CaCO\(_3\) per coat. Sodium chloride and hypochlorite are removed by dropping the 50% caustic solution through a column of 50% NH\(_4\)OH.

2.4.7 Chlorine Drying

The hot chlorine evolved from the anode compartment contains much water vapour. It is therefore, cooled to condense most of the water vapour and further dried in a sulfuric acid scrubber. A stoneware tower or stainless steel tower with acid proof packing should be used. Wet chlorine is also handled in polyester, PVC or similar resistance material. After drying, iron and steel tower can be used as discuss earlier. The dried Cl\(_2\) is compressed between 35 to 80 psi by one of the following temperature pressure combination.

1. High pressure (9-10 atm.), water cooling
2. Medium pressure (2-3 atm.), refrigeration at -20°C
3. Low pressure (3-10 cm Hg), refrigeration at -40°C

**Rotary compressors** with H\(_2\)SO\(_4\) seals have been used for liquefaction process. The heat of compression is progressively removed by water and finally by refrigeration to about -20F, when all the chlorine should be liquefied. It is further cooled -50F and the liquid chlorine is led to a steel storage tank and then filled in steel cylinder of 50-100 kg capacity for sale.

2.4.8 Hydrogen

Hydrogen evolved at the cathode is either burnt for boiler fuel or used as hydrogen source.
2.5 LIME SODA PROCESS FOR THE MANUFACTURE OF CAUSTIC SODA

2.5.1 Kinetics

Caustic soda is also manufactured by making use of lime soda process. In this process caustic soda is formed by the reaction between sodium carbonate and milk of lime.

\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3 \]

The above reaction never reaches completion and an equilibrium is set up, which depends upon the solubility of the sparingly soluble \( \text{CaCO}_3 \). There are always some calcium hydroxide and calcium carbonate present in solid phase, when equilibrium state is attained.

\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3 \, [\text{Solid}] \]

With the progress of forward reaction, the concentration of \( \text{CO}_3^{2-} \) ions decreases and solubility of \( \text{CaCO}_3 \) increases. This begins the backward reaction until equilibrium is attained. In the beginning, the concentration of \( \text{CO}_3^{2-} \) ions is very high and hence the solubility of \( \text{CaCO}_3 \) is extremely small. At equilibrium, the rate of forward reaction is equal to the rate of backward reaction. Hence according to law of mass action

\[ K_1 \left[ \text{Ca}^{+2} \right] [\text{OH}^-]^2 = K_2 \left[ \text{Ca}^{+2} \right] [\text{CO}_3^{2-}] \]

\[ K = \frac{K_2}{K_1} = \frac{\left[ \text{Ca}^{+2} \right] [\text{OH}^-]^2}{\left[ \text{CO}_3^{2-} \right]} \]

It is therefore evident that in order to have high conversion (i.e. \( \text{OH}^- \) high), the soda ash solution should be dilute [\( \text{CO}_3^{2-} \) less]. In actual case, with an initial concentration of \( \text{Na}_2\text{CO}_3 \) is 10%, there is about 95% conversion, whereas with 20% \( \text{Na}_2\text{CO}_3 \) there will be less conversion.

The heat of reaction \( \Delta H \) is about 2100cals which is not appreciable, the value of \( K \) and therefore, equilibrium is not appreciably altered by change in temperature. An increase in temperature, however, increases the setting of \( \text{CaCO}_3 \) and the rate of reaction. In the practice, the reaction is carried out at the boiling point of the solution.

It should be noted that \( \text{Na}_2\text{CO}_3 \) solution should not be very dilute because in case of less concentrated solution, the caustic soda produced will also be very dilute and thus it will involve a higher cost of concentration. In case of more concentrated solution, the loss of \( \text{Na}_2\text{CO}_3 \) becomes appreciable. Hence 10% solution of sodium carbonate is used which is supposed to be neither too dilute nor too concentrated.

2.5.2 Manufacture

A 20% solution of soda ash made with weak liquor from a previous stage is mixed with milk of lime or slaked lime in the desired proportion and then fed into a causticizer tank, called agitator. The causticizer tank is fitted with a mechanical stirrer and consists of a steam line to heat the mixture to 80–90°C. Agitation may also be carried out with compressed air instead of stirrer.

After the equilibrium is reached, the liquid is allowed to settle for 2-3 hours. The clear liquid containing about 10% \( \text{NaOH} \) is drawn by a swing pipe. The sludge is washed in counter current manner with the washing of the previous operation. The causticising process is completed in the series of three agitators. The mixture of \( \text{NaOH} \) and \( \text{CaCO}_3 \) from the last
agitator to the first Door thickener, which consist of a large shallow cylindrical tank into which the slurry is fed at the center. The over flow liquid from the first thickener is filtered and filtrate containing 10-11% NaOH is evaporated to 50 % solution in a triple effect vacuum evaporator as described earlier. The solid CaCO₃ is gradually settles to the bottom. At least three thickeners are used in series. The lime sludge from the bottom of the first thickener is washed with the water. The filtrate from the next operation (filtering in a drum vacuum filter) is also added to the second thickener, where the liquor is treated with excess of weak soda solution. The overflow from the second thickener is used as a weak liquor to make soda ash solution. The lye suspension from the second agitator is settled in the second thickener is filtered through rotary drum vacuum filter and passed to a third thickener where it is finally washed with fresh water to remove any traces of NaOH. The slug of the filter cake (CaCO₃) is return in the lime kiln to from lime. The caustic soda (11 % strength) contains small amount of NaCl and Na₂CO₃.

2.5.3 Properties
- It is hygroscopic in nature
- Melting point: 318°C

2.5.4 Uses
It is an important heavy chemical and occupies among the basic chemicals position equal in importance to sulfuric acid and ammonia. It is used in soap, rayon, dyes, paper, drugs, foods, rubber, textiles, chemicals, bleaching, metallurgy and petroleum industries.

2.6 CHLORINE

Chlorine can be manufacture by several methods such as electrolysis, Deacon’s, heating of auric acid and platonic chloride. All methods except electrolysis are costly. So, chlorine is largely manufacture by electrolysis process.

2.6.1 Manufacture of chlorine using diaphragm cells
Chlorine can be obtained as co-product during the manufacture of caustic soda by electrolysis process.

2.6.1.1 Raw material
The main raw material for the manufacture of chlorine by electrolytic method is the common salt of required purity.

2.6.1.2 Brine purification
Commercial sodium chloride usually contains impurities such as calcium, magnesium and iron compounds. So, the brine purification is necessary for getting pure caustic soda and to decrease clogging of the cell diaphragm by insoluble hydroxides formed during electrolysis. These impurities are removed by adding lime and soda ash, when insoluble carbonates and hydroxides are precipitated. Sometimes sulfate are removed with BaCl₂ or the hot brine is treated with OH⁻ and CO₃²⁻ ions. The clear brine is neutralized with hydrochloric acid. After treatment for purification the brine is allowed to settle. The brine saturated with NaCl at 60°C is fed into the cell containing 324gms/liter of NaCl. The electrolysis is carried out in diaphragm cells; each cell usually required 3.0-4.5 volts. A number of them are put in series to increase the voltage of a given group.

2.6.1.3 Brine Electrolysis
Brine electrolysis is carried out with an anode current density of 0.07amp/cm². As a result of electrolysis Na⁺ ions move to the cathode, where H⁺ ions and OH⁻ ions are also formed as a result of reduction of water. On the other hand Cl⁻ ions are directed towards the anode, where they lose one electron each and are thus liberated as chlorine atoms, which unite immediately to form chlorine molecules and hence chlorine gas at the anode. Since the discharge potential of chlorine ions is lower than that of OH⁻ ions, Cl⁻ ions are discharge at the anode and OH⁻ ions are remain in solutions. Similarly the discharge potential of Na⁺ is greater than H⁺ ions hence H⁺ ions are discharge at the cathode, while Na⁺ ions remain in the solutions.

\[
\text{NaCl} \iff \text{Na}^+ + \text{Cl}^- \\
2\text{H}_2\text{O} + 2\text{e}^- \iff \text{H}_2 + \text{OH}^-
\]
At cathode: 
\[ 2H_2O + 2e^- \rightarrow H^+ + 2OH^- \]
\[ Na^+ + OH^- \rightarrow NaOH \]
Since chlorine attack caustic soda solution even in the cold, formed sodium chloride and hypochlorite, it is necessary that the construction of the cell should be such that NaOH and Cl\(^{-}\) once formed do not come in direct contact with one another.

2NaOH + Cl\(_2\) \rightarrow NaCl + NaClO + H\(_2\)O

2.6.1.4 Chlorine Drying

The hot chlorine evolved from the anode compartment contains much water vapour. It is therefore, cooled to condense most of the water vapour and further dried in a sulfuric acid scrubber. A stoneware tower or stainless steel tower with acid proof packing should be used. Wet chlorine is also handled in polyester, PVC or similar resistance material. After drying, iron and steel tower can be used as discuss earlier. The dried Cl\(_2\) is compressed between 35 to 80 psi by one of the following temperature pressure combination.

1. High pressure (9-10 atm.), water cooling
2. Medium pressure (2-3 atm.), refrigeration at -20\(^\circ\)C
3. Low pressure (3-10 cm Hg), refrigeration at -40\(^\circ\)C

Rotary compressors with H\(_2\)SO\(_4\) seals have been used for liquefaction process. The heat of compression is progressively removed by water and finally by refrigeration to about -20\(^\circ\)F, when all the chlorine should be liquefied. It is further cooled -50\(^\circ\)F and the liquid chlorine is led to a steel storage tank and then filled in steel cylinder of 50-100 kg capacity for sale.

2.6.2 Deacon’s method for the manufacture of chlorine

In this method hydrochloric acid is partially oxidizes to chlorine by heating of HCl gas with oxygen (air) at 400-450\(^\circ\)C in presence of porous earthenware impregnated CuCl\(_2\) as catalyst.

\[ 4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O \]

OR
\[ 2CuCl_2 \rightarrow 2CuCl + 2Cl_2 \]
\[ 4CuCl + O_2 \rightarrow 2CuCl_2 + 2Cl_2 \]
\[ Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O \]

Cl\(_2\) mixed with unconverted HCl and system is washed with cold water and dried with concH\(_2\)SO\(_4\) as described earlier. This is an old method for manufacture of chlorine and is not in used now.

2.6.3 Other methods

Pure chlorine can also be prepared by heating Auric chloride, AuCl\(_3\) or platonic chloride, PtCl\(_4\) in a hard glass tube.

\[ 2AuCl_3 \rightarrow 2AuCl + 2Cl_2 \] 175\(^\circ\)C 190\(^\circ\)C
\[ 3AuCl_3 \rightarrow 3AuCl + 3Cl_2 \] 375\(^\circ\)C 600\(^\circ\)C
\[ PtCl_4 \rightarrow PtCl_2 + Cl_2 \]

These method are, however very costly and not used in the manufacture of chlorine. Chlorine is largely manufactured by the electrolytic processed as described earlier.

2.6.4 Properties

- Boiling point: -34\(^\circ\)C
- Melting point: -101\(^\circ\)C
- Vapour density: 2.48 (v/s air)
- Vapour pressure: 4800mmHg (20\(^\circ\)C )

2.6.5 Uses

It is obtained as byproduct in the manufacture of caustic, soda, finds applications in paper and pulp, solvents, explosives, plastics, pesticides, sanitation and various chemical industries.
2.7 SODA ASH

Soda ash or sodium carbonates the most important high tonnage, low cost, reasonably pure, soluble alkali available to the industries as well to the laboratory. Soda ash, commonly known as sodium carbonate is manufactured by making use of following process. 
1. Leblanc process. 
2. Solvay’s ammonia soda process. 
3. Dual process (modified Solvay’s process) 
4. Electrolytic process.

2.8 LEBLANC PROCESS

This producer is only of historical importance, because this method has now been replaced completely by Solvay process or modified by Solvay process.

2.8.1 Raw material

This raw materials used are common salt (NaCl), sulfuric acid, limestone and coke.

2.8.2 Manufacture

Common salt is first mixed with the calculate amount of concentrated sulfuric acid (equivalent quantities of both) and then heated in a cast iron salt cake furnace by flue gases from adjacent coal of fire. Hydrochloric acid gas is given off which is allow to pass up a tower packed with coke. A spray of water also comes down the tower and dissolved the vapours of HCl to a hydrochloric acid. Sodium hydrogen sulfate is formed as a pasty mass accordingly to the reaction.

\[ \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl} \]

The paste of NaHSO₄ is taken out and heated to a high temperature on the hearth of a furnace along with some more common salt. The sodium hydrogen sulfate is thus converted into sodium sulfate, known as salt cake.

\[ \text{NaHSO}_4 + \text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl} \]

The salt cake is broken or pulverized, mixed with coke and limestone and charged into black ash rotary furnace consisting of refractory lined steel shells. The mass is heated by hot combustion gases entering at one end and leaving at the others. The molten porous of gray mass (known as, black ash) thus formed is separated from the calcium sludge and then crushed and leached with water in absence of air in a series of iron tank working on the principal of counter currents.

\[ \text{Na}_2\text{SO}_4 + 4\text{C} \rightarrow \text{NaS} + 4\text{CO} \]

\[ \text{Na}_2\text{S} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaS} \]

(Black ash sludge)

The extract containing sodium carbonate, sodium hydroxide, and other impurities is sprayed from the top of a tower counter current to flow of hot gases from the black ash furnace. The sodium carbonate thus obtained is concentrated in open pans and then cooled to get sodium carbonate. The product is calcined get soda ash which is recrystallized to get the crystals of Na₂CO₃.10H₂O. The sludge containing mostly CaS is left behind as alkali waste.

The liquor remaining after removal of first batch of soda ash crystals is purified to remove of ion and then causticized with lime to produce caustic soda. Leblanc process has now an obsolete method and sodium carbonate is now manufactured mostly by Solvay’s process.

Recovery of sulfur from alkali waste

The freshly prepared alkali waste is charged into cylindrical iron vessels arranged in series and CO₂ delivered from lime kilns is passed through

\[ \text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{S} \]

\[ \text{CaS} + \text{H}_2\text{S} \rightarrow \text{Ca(HS)}_2 \]

\[ \text{Ca(HS)}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{S} \]
The H₂S gas thus obtained is then conducted together with a regulated amount of air in a Claus kiln containing in iron oxide as catalyst

\[
\text{H}_2\text{S} + \text{O} \rightarrow \text{H}_2\text{O} + \text{S}
\]

The reaction is exothermic and proceeds without further external heat. Sulfur recovered in this manner is used in the manufacture of sulfuric acid.

2.9 SOLVAY'S AMMONIA SODA PROCESS

2.9.1 Raw material
Salt, limestone and coke are the main raw materials. Ammonia as a catalyst which enters in to the chemical combinations and is recovered, and only a small amount is lost (About 99.8% is recovered). Salt is used as brine pumped from deep wells or as crystalline salt obtained from evaporation methods. The most suitable limestone is hard and strong. It should be free from impurities, such as silica.

- **Basis:** 1 ton of Na₂CO₃ (58% N₂O)
- **Salt (NaCl):** 1.55 tonnes
- **Cooling water:** 40 – 60 tonnes
- **Lime stone:** 1.20 tonnes
- **Electricity:** 210 KWH
- **Coke:** 0.09 tonnes
- **Plant capacity:** 200 – 2000 tonnes/day
- **Ammonia losses:** 1.5 kg

2.9.2 Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH in k.cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CaCO₃ → CaO + CO₂</td>
<td>+43.4</td>
</tr>
<tr>
<td>2. C(s) + O₂(g) → CO₂(g)</td>
<td>-96.5</td>
</tr>
<tr>
<td>3. CaO(s) + H₂O(l) → Ca(OH)₂(aq)</td>
<td>-15.9</td>
</tr>
<tr>
<td>4. NH₃(aq) + H₂O(l) → NH₄OH(aq)</td>
<td>-8.4</td>
</tr>
<tr>
<td>5. 2NH₄OH + CO₂ → (NH₄)₂CO₃ + H₂O</td>
<td>-22.1</td>
</tr>
<tr>
<td>6. (NH₄)₂CO₃ + CO₂ + H₂O → 2NH₄HCO₃</td>
<td></td>
</tr>
<tr>
<td>7. NH₄HCO₃ + NaCl → NH₄Cl + NaHCO₃</td>
<td></td>
</tr>
<tr>
<td>8. 2NaHCO₃ → Na₂CO₃ + CO₂ + H₂O</td>
<td>30.7</td>
</tr>
<tr>
<td>9. 2NH₄Cl + Ca(OH)₂ → 2NH₃ + CaCl₂ + 2H₂</td>
<td>10.7</td>
</tr>
</tbody>
</table>

**Overall reaction**

CaCO₃ + 2NaCl → Na₂CO₃ + CaCl₂

-24.4

2.9.3 Manufacture

The principal of Solvay's method is based on the fact that ammonia is dissolved in a salt solution and then ammoniate brine solution is allowed to react with CO₂ obtain by calcining lime stone with coke. A precipitate of NaHCO₃, thus obtain is then calcined to produce high purity Na₂CO₃.

2.9.4 Preparation and purification of brine

The salt used in the process is saturated solution of NaCl which is obtained as natural or artificial brine pumped from a wells. The brine is purified and remove calcium sulfate, magnesium and iron salt by adding sodium carbonate and sodium hydroxide. The precipitated carbonates and hydroxide are removed by filtration. The saturated salt brine may also be purified be in a series of washer towers with dilute ammonia and then with CO₂ to remove calcium, magnesium and iron salts. The brine is purified by allowing it to settle in vats, as a result if which precipitated calcium carbonate, magnesium carbonate and hydroxide and iron hydroxide settle down and pure brine solution is pumped to the ammonia absorber tower, where it dissolve NH₃ with the liberation of heat.

2.9.5 Ammoniation of Brine

The purified brine is allowed to percolate down the strong ammonia tower in which ammonia gas is passed through the bottom. The brine and ammonia thus meet in a counter current fashion. The brine solution thus takes up the necessary amount of ammonia. Much heat is liberated in this process as shown by reaction (5). The gas which escapes solution in the tank is absorbed by the brine falling down the tower. Some carbon dioxide is also absorbed by ammonia, as a result of which some insoluble carbonate is also precipitated. The
ammoniated brine is allowed to settle, coded to about 30°C and pumped to the carbonating tower.

**2.9.6 Lime kiln**

CO₂ is obtained along with CaO by calcining limestone mixed with coke in a lime kiln. In this manner more of CO₂ is formed as a result of burning of coke necessary to supply necessary heat required for the decomposition of lime stone.

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO + CO}_2 \quad \Delta H = -43.4 \text{ kcal} \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \quad \Delta H = -96.5 \text{ kcal}
\end{align*}
\]

The calcium oxide obtained from the lime kiln is converted into slaked lime and then pumped directly to the ammonia recovery tower.

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \Delta H = -15.9 \text{ kcal}
\]

**2.9.7 Carbonation of ammonium brine**

Carbon dioxide obtained from the lime kiln is first compressed and then passed through the bottom of carbonating tower down which ammoniated brine percolates. Carbonating towers are about 22-25 m height, 1.6-2.5 m in diameter and constructed of cast iron. They operate in series with several precipitating towers. During the precipitation cycle, the temperature gradient is maintained about 20-25°C at the both ends and 45-55°C at the middle by making use of cooling coils, provided with the tower at about 20 ft. above the bottom. The tower gradually becomes fouled as sodium bicarbonate cakes on the cooling coils and shelves. The cooling coils of the fouled tower are shut off and a fresh solution of ammoniated brine is fed down the tower. The sodium bicarbonate deposits are dissolved in the hot incoming ammoniated brine and a solution of ammonium carbonate is formed. This ammonium carbonate solution with some unconverted NaHCO₃ is allowed to fall down a second tower, called making tower, along with ammoniated brine (which was previously washed) and rich carbon dioxide (90-95%) gas from the bicarbonate calciner is recompressed and pumped to the bottom of the making tower. The ammonium carbonate first reacts with CO₂ to form ammonium bicarbonate and the latter reacting with salt, forms sodium bicarbonate.

\[
\begin{align*}
(\text{NH}_4\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}) & \rightarrow 2\text{NH}_4\text{HCO}_3
\end{align*}
\]

The reaction is exothermic and so the heat of reaction is removed by cooling coils.

\[
\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}
\]

The making towers are constructed with a series of boxes and sloped baffles so that the precipitate of NaHCO₃ is passed to a rotary filter.
2.9.8 Filtration
The slurry is then filtered on a rotary vacuum filter. The vacuum filter helps in drying bicarbonate and in recovering ammonia. The cake is then washed on a centrifugal filter to remove the moisture or calcined directly. During washing, about 10% NaHCO₃ also passes into filtrate. The filtrate containing NaCl, NH₄Cl, NaHCO₃ and NH₄HCO₃ is treated with lime obtained from lime kiln to recover NH₃ and CO₂. These are re-circulated and used again in the purification of brine.

2.9.9 Calcination
The washed, moist NaHCO₃ from the drum filter is calcined at about 200°C in a calciner, which may be gas fired or a steam heated unit.

\[ 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

The calciner is horizontal and is fired at the feed end, the heating being through the shell parallel to the product, which prevent the tendency of the bicarbonate to cake into lumps.

The hot soda ash form the calciner is passed through a rotary cooler and packed in bags. The exit gases (CO₂, NH₃, steam etc.) are cooled and condensed to get liquid ammonia; the rich CO₂ gas is cooled and returned to the carbonating tower. The product from the calciner is light soda ash. To produce dense soda ash, sufficient water is mixed with it to form more mono hydrate Na₂CO₃.H₂O and the mixture is recycled.

2.9.10 Recovery of ammonia
The ammonia is recovered in a distillation column, called strong ammonia liquor still, consisting of two parts. The top part above the lime inlet is called heater, while the bottom part below the lime inlet is called as lime still. The filtrate obtained from washing of NaHCO₃ from the pressure type rotary filter is fed into the heater, where free ammonia and carbon dioxide are driven off by distillation. Dry lime or milk of lime (slaked lime) obtained from lime kiln is fed through the lime inlet and mixed with the liquor from the upper part or heater. As the liquor flows down the column, calcium chloride and calcium sulfate are formed and NH₃ gas is released.

\[ \text{NH}_4\text{Cl} + \text{Ca} (\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O} \]
\[ (\text{NH}_4)_2\text{SO}_4 + \text{Ca} (\text{OH})_2 \rightarrow \text{CaSO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O} \]

The liquor from the bottom of the lime still is free from ammonia and contains unreacted NaCl and largely CaCl₂, which is disposed off. The liquor is, therefore allowed to settle in settling ponds and the clear liquid is evaporated till the salt separates out and is sold as such for calcium chloride or further evaporated.

2.9.11 Properties
99% sodium carbonate (58% Na₂CO₃) is known as light soda ash (solid density 1.86). Dense soda ash has solid density of 1.91. Both grades (lighty and dense) are granular. Melting point is 851°C. Na₂CO₃. 10H₂O is known as washing soda.

2.9.12 Uses
It is widely used in the manufacture of glass, sodium bicarbonate, caustic soda, soap pulp and paper, textiles, chemical, petroleum, dyes. It is also used in foods, leather and water softening industries.

2.10 SODIUM BICARBONATE

2.10.1 Manufacture
Sodium bicarbonate or baking soda is manufactured by passing a saturated solution of soda ash from the top of a tower similar to the carbonating tower in soda ash manufactured by Solvay process. Compressed CO₂ gas is admitted in the tower from the bottom and the temperature of the tower is maintained at 40°C by the cooling coils, provided above the bottom of the tower. The suspension of bicarbonate formed is removed from the bottom of the tower, filtered and washed on a vacuum rotary drum filter. After centrifugation, the bicarbonate is dried on a continuous belt conveyor at 70°C to get 99.9% pure sodium bicarbonate.

\[ \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 \]
It should be noted that sodium bicarbonate is not manufactured by refining the crude \( \text{NaHCO}_3 \) obtained from the vacuum drum filters of the reasons are:

- It is very difficult to dry this bicarbonate completely.
- The value of the ammonia in this crude \( \text{NaHCO}_3 \) would be lost.
- Even small traces of ammonia associated with it renders it unfit for many uses.
- The bicarbonate formed by this process would not be as pure as obtained by above method.

2.10.2 Uses

Sodium bicarbonate is used in the manufacture of backing powder, carbonated water, leather goods and in the fire extinguishers.

2.11 BAKING POWDERS

The leavening agents are the substances used first to produce aeration and lightness in breads and cakes. Some form of yeast, or ferment acting carbohydrates of the flour giving CO\(_2\) and an alcohol, the the first of the leavening agent used. Later on, baking soda or sodium bicarbonate, \( \text{NaHCO}_3 \) was widely used, but because it often impetrated an unpleasant taste or even a yellowish colour due to alkalinity of the sodium carbonate formed, the search for better reagents continued.

Baking powders consist of a dry mixture of sodium bicarbonate with one or more chemicals capable of completely decomposing it. The principal backing acids used are monocalcium phosphate monohydrate, anhydrous monocalcium phosphate, sodium acid pyrophosphate, sodium aluminum sulphate, tartaric acid and the acid tartrates. However, monocalcium phosphates have widely been used. A filler or drying agent, such as starch or flour, is usually added to the active ingredients to give a better distribution throughout the dough and to serve as diluents or preventive of the reaction until water and heat are applied. The actions of different, backing powders can be represent, by the following equations:

\[
\begin{align*}
\text{Na}_2\text{Al}_2(\text{SO}_4)_4 + 6\text{NaHCO}_3 & \rightarrow 6\text{CO}_2 + 4\text{Na}_2\text{SO}_4 + 2\text{Al(OH)}_3 \\
3\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 8\text{NaHCO}_3 & \rightarrow 8\text{CO}_2 + \text{Ca}_3(\text{PO}_4)_2 + \text{NaHPO}_4 + 11\text{H}_2\text{O} \\
\text{KH}_2\text{PO}_4 + \text{NaHCO}_3 & \rightarrow \text{CO}_2 + \text{KNaHPO}_4 + \text{H}_2\text{O} \\
\text{NaH}_2\text{PO}_4 + \text{NaHCO}_3 & \rightarrow \text{CO}_2 + \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} \\
\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + 2\text{NaHCO}_3 & \rightarrow 2\text{CO}_2 + 2\text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} \\
\text{KHC}_4\text{H}_4\text{O}_6 + \text{NaHCO}_3 & \rightarrow \text{KNaC}_4\text{H}_4\text{O}_6 + \text{CO}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

Most baking powders are so made that contain 26-29% \( \text{NaHCO}_3 \) and enough of acid ingredients to decompose the bicarbonate and 14-15% \( \text{CO}_2\). The rest of powder, 20-40%, consists of cornstarch of flour.

2.12 SODIUM HYPOCHLORITE

2.12.1 Manufacture

Sodium hypochlorite \( \text{NaOCl} \) is prepared by the electrolysis of solution of \( \text{NaCl} \) in an undivided cell at a temperature below 24°C. Sodium hydroxide liberated at the cathode reacts with chlorine liberated at the anode to give sodium hypochlorite.

\[
2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}
\]

The type of electrolytic cell commonly employed for the manufacture of \( \text{NaOCl} \) is shown in the figure.

![Fig. 10. Electrolytic cell for the preparation of bleaching solution.](image)
It consists of two semi porcelain rectangular vessels X and Y, are placed inside the other. The inner smaller vessel X is fitted with 30 vertical and transverse graphite electrode face to face so that the vessel is divided into 30 compartments. The electrodes are closed to one another, joined in series. The extreme electrodes are connected with the positive and negative terminals of 110 volt main. On passing current in the bipolar cell, each of the outlet electrode acts as a cathode on one face and anode on the other face due to induction. In each compartment, the left hand side of the left hand electrode acts as the cathode, and the opposite side of the right electrode acts as the cathodes and the opposite of the right hand side electrode acts as the anode. The inner vessel X is placed in the outer big vessel Y with pure NaCl solution, so that two vessels almost completely filled up with the solution of NaCl. Cold water is continuously circulated through a cooling coil immersed in the solution on the right hand side in the bigger vessel Y. The temperature of the solution is kept below 24°C by circulating cold water through the cooling coil.

On passing current, NaOH and H₂ are formed on the cathodes and Cl₂ is formed at the anode. Since the cell is undivided, NaOH liberated at cathode reacts with chlorine liberated at anode and mixture of NaOCl (called bleaching mixture) is formed according to above reaction. As the hydrogen liberated at the cathodes, bubbles through the solution in vessel X, the solution (NaOCl + NaCl) overflows in the outer vessel Y and simultaneously some fresh solution of NaCl get sucked from Y in the inner vessel X through the holes at sides. The circulation of electrolyte continues until electrolysis complete.

2.12.2 Uses

Sodium hypochlorite is used as a disinfectant as well as deodorant dairies, creameries, water supplies and sewage disposal. It is also used as a bleaching agent and is very useful on cotton, linen, jute artificial silk and pulp.